⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　平4-94094

⑤Int. Cl.⁵　識別記号　庁内整理番号　⑬公開　平成4年(1992)3月26日

H 05 B 33/18　8815-3K
33/20　8815-3K

審査請求　未請求　請求項の数　5　（全8頁）

⑭発明の名称　薄膜ＥＬ素子

㉑特　願　平2-210467

㉒出　願　平2(1990)8月10日

⑫発明者　高橋　小弥太　神奈川県相模原市相模大野7-37-17
⑫発明者　渋谷　孝二　神奈川県座間市南栗原4-3-1
⑫発明者　近藤　昭夫　愛知県江南市東野土手5-10
⑪出願人　東ソー株式会社　山口県新南陽市開成町4560番地

明　細　書

1．発明の名称

薄膜ＥＬ素子

2．特許請求の範囲

(1) ＥＬ発光層及び該ＥＬ発光層に電圧を印加する手段を有してなる薄膜ＥＬ素子において、ＥＬ発光層が、ＭｇＳ、ＣａＳ、ＳｒＳ又はＢａＳを母体とし、該母体中にＬａ、Ｃｅ、Ｐｒ、Ｎｄ、Ｓｍ、Ｇｄ、Ｔｂ、Ｄｙ、Ｈｏ、Ｅｒ、Ｔｍ、Ｙｂ及びＬｕよりなる群から選択された少なくとも一種以上の希土類金属及びＰを含有する薄膜を含み、該薄膜中の上記希土類金属の合計の濃度が０．０３～３．０atm%、Ｐの濃度が上記希土類金属の合計の濃度に対して１．３～４．０倍であることを特徴とする薄膜ＥＬ素子。

(2) ＥＬ発光層が、ＣａＳを母体とし、該母体中にＣｅ及びＰを含有する薄膜を含み、該薄膜中のＣｅの濃度が０．０３～０．４atm%、Ｐの濃度が上記Ｃｅの濃度に対して１．３～４．０倍であることを特徴とする請求項第(1)項に記載の薄膜ＥＬ素子。

(3) ＥＬ発光層が、ＳｒＳを母体とし、該母体中にＣｅ及びＰを含有する薄膜を含み、該薄膜中のＣｅの濃度が０．０３～０．４atm%、Ｐの濃度が上記Ｃｅの濃度に対して１．３～４．０倍であることを特徴とする請求項第(1)項に記載の薄膜ＥＬ素子。

(4) ＥＬ発光層が、ＳｒＳを母体とし、該母体中にＣｅ、Ｅｕ及びＰを含有する薄膜を含み、該薄膜中のＣｅの濃度が０．０４～０．４atm%、Ｅｕの濃度が０．０１～０．０３atm%、Ｐの濃度が上記Ｃｅの濃度に対して１．３～４．０倍であることを特徴とする請求項第(1)項に記載の薄膜ＥＬ素子。

(5) ＥＬ発光層が、ＳｒＳを母体とし、該母体中にＣｅ及びＰを含有する薄膜とＭｎを含有するＺｎＳ薄膜を積層してなり、上記ＳｒＳを母体とする薄膜中のＣｅの濃度が０．０３～０．４atm%、

Pの濃度が上記Ceの濃度に対して1．3～4．0倍であり、上記ZnS薄膜中のMn濃度が0．1～1．0at%であることを特徴とする請求項第(1)項に記載の薄膜EL素子。

3．発明の詳細な説明

［産業上の利用分野］

本発明は電圧を印加することにより発光を呈するEL（エレクトロルミネッセンス）発光層を有してなる薄膜EL素子に関し、特に多色発光を有する平面ディスプレイに好適な薄膜EL素子に関する。

［従来の技術］

薄膜EL素子は、全固体薄型でコントラストの高い高品質の表示ができる等の優れた特徴をもつ。このような薄膜EL素子の有するEL発光層の材料としては一般に黄橙色発光を呈するMnを含有するZnSが知られており、これは既に実用化され、計測機器、各種情報機器への応用が進んでいる。また、近年より多くの情報を表示するために、多色あるいは、フルカラー表示の可能な薄膜EL素子が望まれ、さかんに研究されている。薄膜EL素子で多色表示をするために、RGB発光を呈するEL発光層が研究されており、その材料としては赤色ではEuを含有するCaS、Smを含有するZnSなどが、緑色ではTbを含有するZnS、Ceを含有するCaSなどが、更に青色ではCeを含有するSrSなどがその対象となっている。また、薄膜EL素子で多色表示をするために、白色発光を呈する薄膜EL素子にカラーフィルターを重ねる方法も提案されており、白色発光を呈するEL発光層の材料としてCe及びEuを含有するSrSあるいはCeを含有するSrS薄膜及びMnを含有するZnS薄膜を積層した材料などが研究されている。

ところで、上述した材料をEL発光層として用いた薄膜EL素子の発光の安定性については従来から様々報告されており、例えばZnS系の材料では、Mnを含有したZnSをEL発光層とした薄膜EL素子は2万～10万時間の安定性が確認されており、Tbを含有するZnSをEL発光層とした薄膜EL素子は1万時間程度の安定性が報告され実用化の一歩手前まできている（昭和63年秋期　第49回応用物理学会学術講演会　講演予稿　p1010）。また、希土類金属を含有したアルカリ土類金属硫化物の材料では、Euを含有したCaSをEL発光層として用いた薄膜EL素子は4KHz駆動で700時間以上発光特性が安定であることが報告されており（昭和61年春期第33回応用物理学会学術講演会　講演予稿　p619）、この値は通常の周波数（30～60Hz）で駆動する条件では5万時間以上に相当する。

一般的に平面型デイスプレイへ薄膜EL素子を適用する場合、通常の周波数（30～60Hz）で駆動する条件で2万～5万時間の発光特性の安定性が要求され、更に具体的には、発光開始電圧の変化が10ボルト以内、駆動電圧での輝度の劣化が20%以内であることが必要である。しかしながら、ZnS系の材料及びEuを含有したCaS以外の材料、特に多色表示をするために必要な材料であるEu以外の希土類金属を含有したアルカリ土類金属硫化物の材料をEL発光層として用いた薄膜EL素子は上記条件を満足するものではなく、その安定性に問題があった。例えば、Ceを含有したSrSをEL発光層とした薄膜EL素子の安定性が報告されているが、この薄膜EL素子は輝度、発光開始電圧の安定性に問題があることが指摘されている（SID　89　ダイジェスト　p321あるいはスプリンガー　プロシーディングス　イン　フィジックス　38巻　エレクトロルミネセンス　132頁など）。

［発明が解決しようとする課題］

本発明の目的は、Eu以外の希土類金属を含有するアルカリ土類金属硫化物をEL発光層として用いた薄膜EL素子において、長時間の安定性を達成せしめることにある。

［課題を解決するための手段］

本発明者らは上記課題を解決するために、鋭意検討を行なった結果、希土類金属を含有するアルカリ土類金属硫化物の母体中にPを添加し、更に母体中の希土類金属の濃度及びP濃度を規定した材料をEL発光層として用いることにより、長時間の安定性を示す薄膜EL素子が得られることを見出だし本発明を完成するに至った。すなわち本発明は、EL発光層及び該EL発光層に電圧を印加する手段を有してなる薄膜EL素子において、EL発光層が、MgS、CaS、SrS又はBaSを母体とし、該母体中にLa、Ce、Pr、Nd、Sm、Gd、Tb、Dy、Ho、Er、Tm、Yb及びLuよりなる群から選択された少なくとも一種以上の希土類金属及びPを含有する薄膜を含み、該薄膜中の上記希土類金属の合計の濃度が0.03～3.0atm%、Pの濃度が上記希土類金属の合計の濃度に対して1.3～4.0倍であることを特徴とする薄膜EL素子である。本発明の薄膜EL素子はEL発光層に特徴のあるものであり、このEL発光層はMgS、CaS、SrS又はBaSのアリカリ土類金属硫化物を母体とし、該母体中に希土類金属及びPを含有する薄膜を含み、かつ該薄膜中の希土類金属及びPの濃度が規定されたものである。ここで、母体中に希土類金属及びPを含有する薄膜を含むEL発光層とは、EL発光層が上記薄膜のみから形成されること、EL発光層が上記薄膜と他の薄膜を積層して形成されることなどを示す。また、本発明において、母体中の希土類金属の濃度は、希土類金属の原子数／母体中の総原子数により規定される。本発明の薄膜EL素子は、EL発光層が上述の薄膜を含むことにより、その輝度において安定性を示すものとなる。なお、その理由は明らかではないが、Eu以外の希土類金属は三価であり、このような希土類金属がアルカリ土類硫化物中に含有する際に生じるアルカリ土類金属欠損がPにより消滅し、またPは硫黄とイオン半径が比較的近いことにあると推測される。また、本発明の薄膜EL素子のEL発光層に含まれるPの濃度は、母体中に含有されるEu以外の希土類金属の合計の濃度に対して1.5～3.0倍であることが更に好ましく、上記範囲の含有量とすることにより、得られる薄膜EL素子は更に高輝度、長寿命となる。

また、本発明の薄膜EL素子において、特にEL発光層が、CaSを母体とし、該母体中にCe及びPを含有する薄膜を含み、該薄膜中のCeの濃度が0.03～0.4atm%、Pの濃度が上記Ceの濃度に対して1.3～4.0倍である薄膜EL素子は高い輝度の安定した緑色発光を呈し、EL発光層が、SrSを母体とし、該母体中にCe及びPを含有する薄膜を含み、該薄膜中のCeの濃度が0.03～0.4atm%、Pの濃度が上記Ceの濃度に対して1.3～4.0倍である薄膜EL素子は高い輝度の安定した青色発光を呈する。更に、EL発光層が、SrSを母体とし、該母体中にCe、Eu及びPを含有する薄膜を含み、該薄膜中のCeの濃度が0.04～0.4atm%、Euの濃度が0.01～0.03atm%、Pの濃度が上記Ceの濃度に対して1.3～4.0倍である薄膜EL素子及びEL発光層が、SrSを母体とし、該母体中にCe及びPを含有する薄膜とMnを含有するZnS薄膜を積層してなり、該積層を構成するSrSを母体とする薄膜中のCeの濃度が0.03～0.4atm%、Pの濃度が上記Ceの濃度に対して1.3～4.0倍であり、上記ZnS薄膜中のMn濃度（Mn原子数／ZnS薄膜中の全原子数）が0.1～1.0atm%である薄膜EL素子は高い輝度の安定した白色発光を呈するので、これにカラーフィルターを重ねることにより、多色表示の可能な薄膜EL素子を得ることができる。

本発明の薄膜EL素子の構造は上述したEL発光層及び該EL発光層に電圧を印加する手段を有していれば特に限定されず、第1図に示す構造のものなどが例示される。第1図において、EL発光層4には透明電極2及び背面電極6により電圧が印加される。また、本発明の薄膜EL素子における発光層の厚みは特に限定されないが、薄膜EL素子の駆動電圧、明るさなどを考慮して0.5～2.5μmとすることが好ましい。

本発明の薄膜EL素子のEL発光層は例えばスパッタリング法、蒸着法、CVD法、MOCVD法、ALE法等種々の薄膜形成技術により形成することができる。このうち、EL発光層を蒸着法により形成する場合、EL発光層の母体となる硫化物に希土類金属及びPを添加した蒸発源が用いられ、蒸発源へのPの添加は種々のリン酸塩、赤リン、リン化ストロンチウムなどのリン化物の添加により行われるが、特に$NH_4H_2PO_4$を用いることが好ましく、これによってEL発光層中のP濃度の調整が容易になる。

また、いずれの成膜法においても、成膜後に真空中、不活性ガス中あるいは硫化水素中で400～700℃の温度で熱処理をすることが好ましく、このことにより得られる薄膜EL素子の発光特性の安定化が促進される。

〔実施例〕

以下、本発明を実施例により示すが、本発明は何らこれらに限定されるものではない。

（実施例1）

第1図に示す薄膜EL素子を次のとおり作製した。はじめに、ガラス基板1の上にフォトエッチングにより透明電極2をストライプ状に形成し、この上に第一絶縁層3を形成した。第一絶縁層3は、厚さ0.03μmのSiO_2薄膜及び厚さ0.17μmのSi_3N_4薄膜をRFスパッタリング法により積層して形成した。次に第一絶縁層3上に厚さ約1.1μmのEL発光層4を形成した。EL発光層4は、SrSに0.08atm%のCe_2S_3と$NH_4H_2PO_4$を混合して成型したペレットを蒸発原料とした電子ビーム蒸着法により形成し、蒸着条件は基板温度を650℃と一定にして、到達真空度を3×10^{-6}Torr以下とし、蒸着中は1×10^{-4}Torrの硫化水素を導入して雰囲気の制御を行ない、堆積速度は5Å／秒とした。その結果、EL発光層中のCe濃度は0.09atm%となった。なお、EL発光層中のP濃度は蒸発原料中の$NH_4H_2PO_4$の含有量を変化させることにより調整した。その後、EL発光層4の上に第二絶縁層5の形成をRFスパッタリング法によりSi_3N_4薄膜を厚み0.15μm、$SrTa_2O_6$薄膜を厚み0.05μm積層して行ない、更にこの上に背面電極6として金属Aℓを0.1μmの厚みで透明電極と直交するように形成して薄膜EL素子を形成した。

次に得られた薄膜EL素子の特性試験を行なった。特性試験にあたり、薄膜EL素子には湿気防止対策として背面ガラスを取り付け、該背面ガラスと薄膜EL素子との空間部分に注入口からシリカゲルを含んだシリコンオイルを注入し、注入口の封止を行なった。また特性試験は、透明電極2と背面電極6との間に1KHz正弦波電圧を印加しながら輝度などを測定する方法で行ない、薄膜EL素子の寿命を測定するためのエージングは、駆動周波数5KHzで初期の発光開始電圧に対して50ボルト高い電圧を印加して行なった。なお、このエージングの条件は、通常の素子駆動条件に対して約100～200倍の加速である。

特性試験として、はじめに得られた薄膜EL素子の発光開始電圧に対して60ボルト高い電圧での輝度（L_{60}）の経時変化測定を行なった。また、経過時間においては薄膜EL素子のエージングを行なった。その測定結果を第2図に示す（初期輝度を1.0に規格化している）。測定の結果、Pを0.12atm%以上含有するEL発光層を有する薄膜EL素子は300時間のエージング後でも初期の80%以上の輝度を保持し、特に0.23atm%のPを含有したものについては1000時間エージング後でも初期の80%以上の輝度を保持していた。

第3図にエージング10時間後に対する300時間後の発光開始電圧の変化量を示す。0.10atm%以上Pを含んだEL発光層を有する薄膜EL素子の発光開始電圧の変化量は10ボルト以内であり、特に0.17atm%以上のPを含んだ試料において発光開始電圧の変化量は4ボルト以内とかなり良好であった。

第4図にEL発光層中のP濃度に対する色度座標の依存性を示す。P濃度の増加に伴い、色度座

様は青色にシフトした。また、薄膜EL素子の輝度の絶対値は、第5図に示すように、初期ではPを含有しないEL発光層を有する薄膜EL素子が高く、24時間エージング以降はP濃度が0.1〜0.2atm%含有するEL発光層を有する薄膜EL素子が最も高かった。

（実施例2）

実施例1と同様の方法で薄膜EL素子を作製した。ただし、EL発光層中のCe濃度を0.1〜0.5atm%とし、CeとPの比が1〜3になるようにして薄膜EL素子を幾種類か作製した。次に得られた薄膜EL素子の5KHz、300時間エージング後のL_{60}を測定した。その結果、P/Ceが1.3以上で300時間エージング後においても初期の80%以上の輝度を保持した。第6図にL_{60}のPとCeの比（P/Ce）に対する依存性を示す（初期輝度を1.0に規格化している）。

また、得られた薄膜EL素子の初期輝度の測定を行なった。第7図にP/Ceが2の場合のEL発光層中のCe濃度に対する初期輝度の依存性を示す。初期輝度はEL発光層中のCe濃度が0.1〜0.2atm%で最も高く、0.4atm%を超えた場合、その半分以下の値となった。

（実施例3）

実施例1と同様の方法でEL素子を作製した。ただし、EL発光層中のCe濃度を0.1atm%、P濃度を0.2atm%となるようにして、発光層4を蒸着した後、5×10^{-6}Torrの真空中において600℃で1時間熱処理を行なって薄膜EL素子を作製した。また、比較のために熱処理を行わない薄膜EL素子も同時に作製した。

第8図にa）熱処理を行わなかった試料とb）熱処理を行った試料の輝度−電圧特性の経時変化を比較して示す。熱処理を行わなかった薄膜EL素子の場合、エージング31時間以降、発光開始電圧の上昇に伴い輝度−電圧特性の傾きが緩やかに減少し、そのためL_{60}の経時変化は、31時間から300時間まで約10%であるが一定電圧での輝度は20%程度低下した。それに対して、熱処理を行った薄膜EL素子では、エージング31時間以降、発光開始電圧は少し上昇したが、輝度−電圧特性はほとんど平行移動した。そのためL_{60}は31時間から300時間まででほとんど変化はなく、一定電圧での輝度の変化でも10%以内であった。

（実施例4）

実施例1と同様の方法でEL素子を作製した。ただし、EL発光層4の母体をCaSとしてCe濃度が0.1atm%、P濃度が0atm%、0.2atm%となるようにして、EL発光層4を蒸着後、5×10^{-6}Torrの真空中において600℃で1時間熱処理を行なった。得られた素子の5KHz、300時間エージング後でのL_{60}は初期のL_{60}に対してP濃度が0atm%の場合20%であり、0.2atm%の場合95%であった。この素子は、高輝度な緑色発光を呈した。

（実施例5）

実施例1と同様の方法でEL素子を作製した。ただし、SrSに添加する希土類金属をPrとし、Pr濃度が0.1atm%、P濃度が0atm%、0.2atm%となるようにして、EL発光層4を蒸着後、5×10^{-6}Torrの真空中において600℃で1時間熱処理を行なった。この素子の初期のL_{60}はEL発光層中のP濃度が0atm%の場合も、0.2atm%の場合もほぼ同じ値であった。また、5KHz、300時間エージング後でのL_{60}は初期のL_{60}に対してP濃度が0atm%の場合55%まで減少した。一方、P濃度が0.2atm%の場合、エージング後20時間まで輝度が急激に上昇し、L_{60}は初期のL_{60}の150%となり、その後も緩やかに輝度が上昇し、300時間エージング後のL_{60}は初期のL_{60}の165%となった。また、発光開始電圧はP濃度に拘らず300時間エージング後において変化量は7ボルト以内であった。

以上の結果より、SrSを母体とし、該母体中にPr及びPを含有したEL発光層を有する薄膜

ＥＬ素子は、発光層中へのＰの添加より、輝度が上昇し、エージングにより安定性が与えられることがわかる。なおこの素子は、高輝度な補色関係のスペクトルをもつ白色発光を呈した。

（実施例６）

実施例１と同様の方法で薄膜ＥＬ素子を作製した。ただし、ＳｒＳに添加する希土類金属をＴｂとしてＴｂ濃度が１．０atm%、Ｐ濃度が０atm%、１．５atm%、２．５atm%となるようにして、ＥＬ発光層４を蒸着後、５×１０$^{-6}$Torrの真空中において６００℃で１時間熱処理を行なった。この素子の５KHz、３００時間エージング後でのL_{60}は初期のL_{60}に対してＰ濃度が０atm%の場合２５％、１．５atm%の場合８３％、２．５atm%の場合９０％であった。この素子は、高輝度な緑色発光を示した。

（実施例７）

実施例１と同様の方法でＥＬ素子を作製した。ただし、ＳｒＳに添加する希土類金属をＣｅ及びＥｕとして、Ｃｅ濃度が０．１atm%、Ｅｕ濃度が０．０２atm%、Ｐ濃度が０atm%、０．１３atm%、０．２atm%となるようにし、ＥＬ発光層４を蒸着後、５×１０$^{-6}$Torrの真空中において６００℃で１時間熱処理を行なった。この素子の５KHz、３００時間エージング後でのL_{60}は初期のL_{60}に対してＰ濃度が０atm%の場合３２％、０．１３atm%の場合８２％、０．２atm%の場合９８％であった。この素子は、高輝度な４５０～７００nmまでの幅広いスペクトルをもつ白色発光を示した。更にこの薄膜ＥＬ素子と赤、緑、青のカラーフィルターを組み合わせることにより、良好な赤、緑、青の発光が得られた。

（実施例８）

実施例１と同様の方法でＥＬ素子を作製した。ただし、発光層４が２層構造になるように、最初に基板温度を２３０℃として電子ビーム共蒸着法によりＭｎを０．４atm%含むＺｎＳ薄膜を０．５μm形成した後、この薄膜上にＳｒＳを母体とし、該母体中にＣｅ及びＰを含有する薄膜を積層した。なお、ＳｒＳを母体とする薄膜は、基板温度を６５０℃として、１×１０$^{-4}$Torrの硫化水素雰囲気で形成し、Ｃｅ濃度を０．１atm%、Ｐ濃度を０atm%、０．２atm%となるように厚み１．０μm蒸着して形成し、その後５×１０$^{-6}$Torrの真空中において６００℃で１時間熱処理を行なった。この素子の５ｋＨｚ、３００時間エージング後でのL_{60}は初期のL_{60}に対してＰ濃度が０atm%の場合５０％、０．２atm%の場合９６％であった。この素子は初期において高輝度な４５０～６５０nmまでの幅広いスペクトルをもつ白色発光を呈した。３００時間エージング後で発光色はＰ濃度が０atm%の場合、Ｃｅを含有したＳｒＳ薄膜からの発光が非常に弱くなり、Ｍｎを含有したＺｎＳ薄膜からの発光色である黄橙色となった。それに対してＰ濃度が０．２atm%の場合３００時間後においても発光色はほとんど変わらず、良好な白色発光を呈し、このＥＬ素子と赤、緑、青のカラーフィルターを組み合わせることにより、高輝度で良好な赤、緑、青の発光が得られた。

［発明の効果］

以上述べたように、本発明の薄膜ＥＬ素子は、多色表示に用いることのできるＲＧＢ発光あるいは白色発光を呈する希土類金属を含有するアルカリ土類金属硫化物をＥＬ発光層とするものであり、その長時間の安定性を達成できたものである。従って、本発明の薄膜ＥＬ素子により、長時間信頼性のある多色発光ＥＬ素子が実現できる。

４．図面の簡単な説明

第１図は、本発明の薄膜ＥＬ素子の構造の一例を示す断面図である。

第２図は、実施例１において行なった本発明の薄膜ＥＬ素子のL_{60}の経時変化の測定の結果を示す図である。

第３図は、実施例１において行なった本発明の薄膜ＥＬ素子のエージング１０時間後に対する

300時間後の発光開始電圧の変化量の測定の結果を示す図である。

第4図は、実施例1において作製した本発明の薄膜EL素子の色度座標を示す図である。

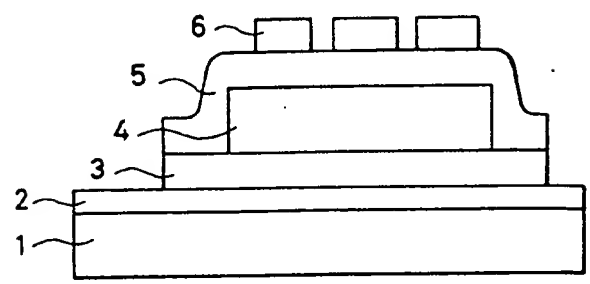
第5図は、実施例1において行なった本発明の薄膜EL素子のエージング初期、24時間後および300時間後の輝度の測定の結果を示す図である。

第6図は、実施例2において行なった本発明の薄膜EL素子の初期のL_{60}と300時間エージング後のL_{60}の測定の結果を示す図である。

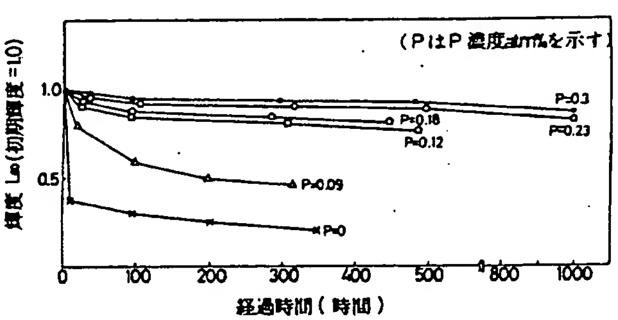
第7図は、実施例2において行なった本発明の薄膜EL素子の初期輝度の測定の結果を示す図である。

第8図は、実施例3において行なった本発明の薄膜EL素子の輝度ー電圧特性の経時変化の測定の結果を示す図である。図中、a)はEL発光層の形成過程において熱処理を行わなかった素子の測定結果、b)は熱処理を行なった素子の測定結果を各々示す。

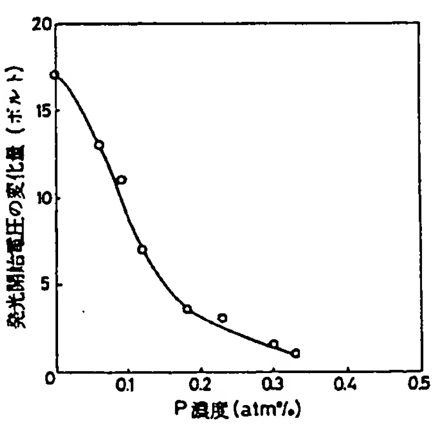
第1図



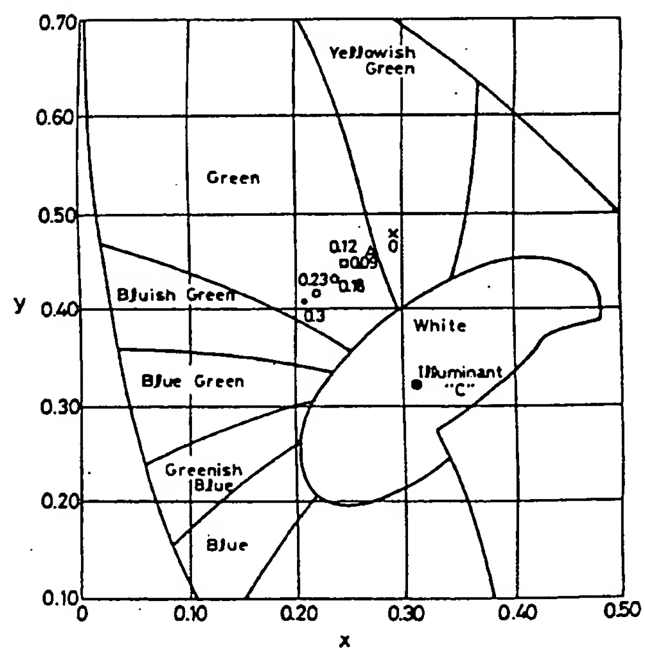
第2図



第3図

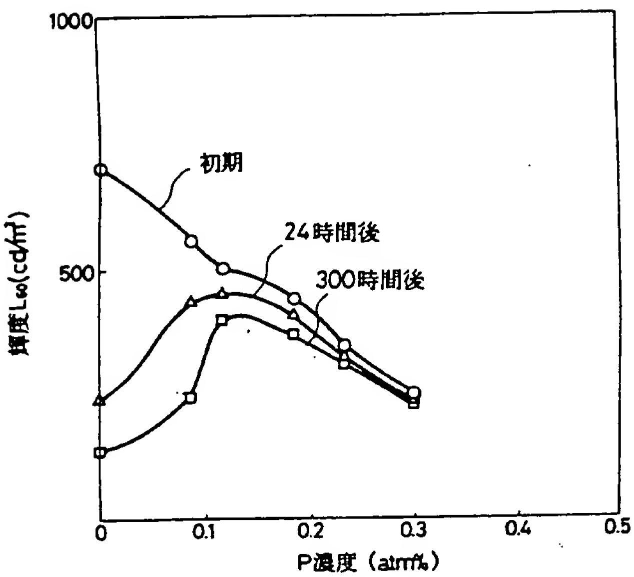


第4図

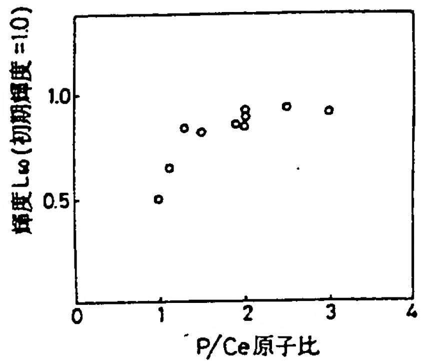


図中数字はP濃度(atm%)

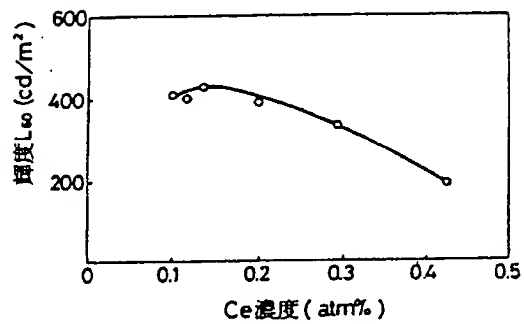
第 5 図



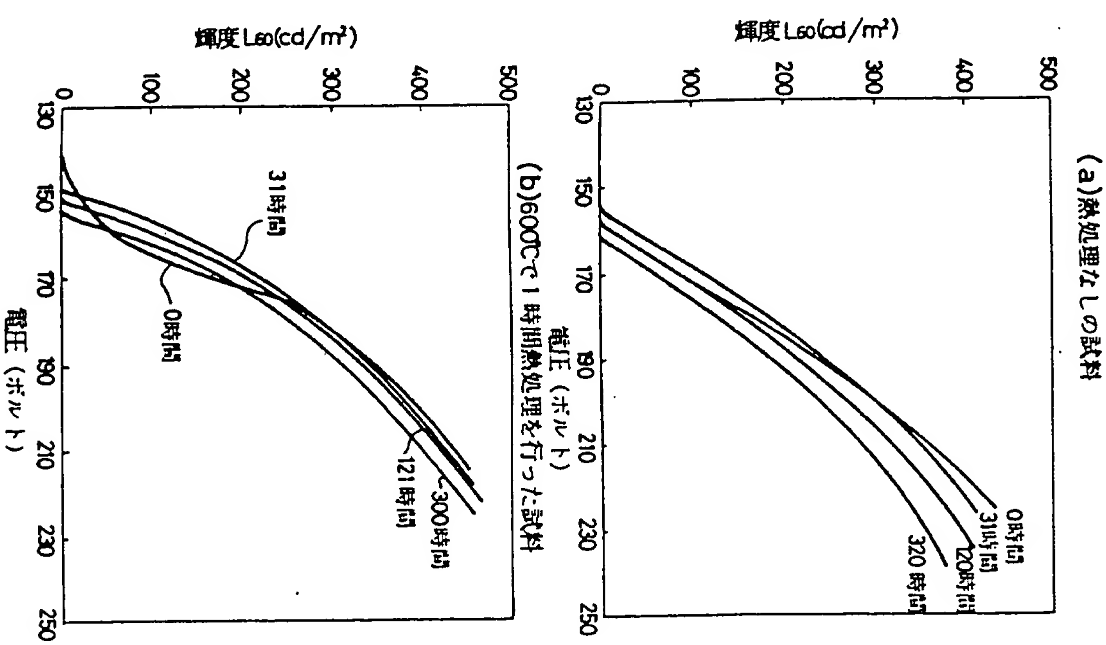
第 6 図



第 7 図



第 8 図



(19) The Patent Office in Japan

(12) Public Patent Report (A)

(11) Patent application number
HEI 4 - 94094

(43) Open date
March 26, 1992

(51) Int.Cl.^{5}	ID symbol	Reference number for the patent office use
H 05 B 33/18		8815-3K
33/20		8815-3K

Request for examination: Examination not requested Number of claims: 5
(Total: 8 pages)

(54) Name of Invention: Thin film EL element

(21) Application number
TOKUGAN HEI 2-210467

(22) Application date
August 10, 1990

(72) Inventor: Koyata Takahashi 7-37-17, Sagami Oono, Sagamihara-shi, Kanagawa-ken

(72) Inventor: Koji Shibuya 4-3-1 Minami Kurihara, Zama-shi, Kanagawa-ken

(72) Akio Kondo 5-10 Higashino Dote, Kounan-shi Aichi-ken

(71) Applicant: Toh-So K.K. 4560-branch, Kaisei-cho, Shin Nanyo-shi Yamaguchi-ken

Details
1. Name of invention
Thin film EL element

2. Range of the patent claim

(1) Concerning the thin film EL element which shall be made by applying the voltage to the EL emission layer and the said EL emission layer, it is the thin film EL element, which shall be characterized by having such EL emission layer, which shall have MgS, CaS, SrS or BaS as the host material, which shall contain the thin film which is composed of P and at least one kind of selected rare earth metal, which are La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and having the total density of the abovementioned rare earth metal within the said thin film to be 0.03 to 3.0 atm%, and having the density of P to be 1.3 to 4.0 times of the total density of the abovementioned rare earth metal.

(2) It is the thin film EL element which is mentioned in Claim (1), which shall be characterized by having such EL element, which shall have CaS as the host material, which shall contain the thin film, which shall contain Ce and P within the host material, and having the density of Ce within the said thin film to be 0.03 to0.4 atm% and having the density of P to be 1.3 to 4.0 times as the density of the abovementioned Ce.

(3) It is the thin film EL element, which is mentioned in Claim (1), which shall be characterized by having such EL element, which shall have SrS as the host material, which shall contain the thin film, which shall contain Ce and P within the host material, and having the density of Ce within the said thin film to be 0.03 to 0.4 atm% and having the density of P to be 1.3 to 4.0 times as the density of the abovementioned Ce.

(4) It is the thin film EL element which is mentioned in Claim (1), which shall be characterized by having such EL element, which shall have SrS as the host material, which shall contain the thin film, which shall contain Ce, Eu and P within the host material, and having the density of Ce within the said thin film to be 0.04 to0.4 atm%, having the density of Eu to be 0.01 to 0.03atm% and having the density of P to be 1.3 to 4.0 times as the density of the abovementioned Ce.

(5) It is the thin film EL element which is mentioned in Claim (1), which shall be characterized by having such EL element, which shall have SrS as the host material, which shall be composed of laminated layers of the thin film, which shall contain Ce and P, and ZnS thin film, which shall contain Mn within the host material, and having the density of Ce within the thin film, which shall have the abovementioned SrS as the host material to be 0.03 to0.4 atm%, having the density of P to be 1.3 to 4.0 times as the density of the abovementioned Ce, and having the density of Mn within the abovementioned ZnS thin film to be 0.1 to1.0 atm%.

3. Detailed explanation of the invention

[Utility field of the industry]

This invention is concerning the thin film EL element, which shall have the EL (electro luminescent) emission layer, which shall indicate the emitting by applying voltage, and it is especially concerning the thin film EL element, which is suitable for the flat display, which shall have multi color emitting.

[Existing technique]

The thin film EL element shall be the solid thin style film, which shall have excellent advantages such as being able to present the high quality and high contrast display. As

for the material of the EL emission layer, which shall contain such thin film EL element, ZnS, which shall contain Mn, which shall produce the yellow orange emission, is commonly known, and it is already made for the practical use, and the practical application for use of the measuring instruments and the numbers of varieties of information equipment are progressing. Also, recently, in order to display even more information, the thin film EL element, which is able to make a multi color display or full color display, is desired, and studying has been done enthusiastically in the area. In order to make a multi display by the thin film EL element, such EL emission layer, which shall produce RGB emitting, has been studied. As for the material for this, ZnS which shall contain Sm or CaS which shall contain Eu, etc., are used for the red color, ZnS which shall contain Tb or CaS which shall contain Ce, etc., are used for the green color, and SrS which shall contain Ce, etc., is used for the blue color. Also, in order to make the multi color display, such methods, such as laminating color filter to the thin film EL element which shall produce the white emitting, shall also be proposed, and as for the material of the EL emission layer which shall produce the white emitting, laminated layers of SrS, thin film which shall contain Ce and Eu, SrS thin film, which shall contain Ce and/or ZnS thin film, which shall contain Mn, have been studied.

By the way, the reader should take note that various reports have been made until now concerning the stability of the emission of the thin film element which the abovementioned material is used for the EL emission layer, for example, concerning the ZnS related material, the stability of 20,000 to 100,000 hours for the thin film EL element has been confirmed when using Mn contained ZnS as the emission layer, and in the case of the thin film EL element which shall have the Tb contained ZnS as the EL emission layer, the stability has been reported as approximately 10,000 hours and it is almost ready to make it practicable (manuscript P.1010 of the 49th Applied Physical Society Technical Lecture Meeting, autumn, 1988). Also, concerning the material of the alkaline earth metallic sulfide which shall contain the rare earth metal, the thin film EL element, which Eu contained CaS is used as for the use of the emission layer, it is reported that the emitting characteristics are stable for at least 700 hours at 4 KHz drive (manuscript P.619 of the 33rd Applied Physical Society Technical Lecture Meeting, spring, 1986), and this value is equivalent to at least 50,000 hours when driving is performed under the normal frequency condition (30 to 60 Hz).

Generally, when thin film EL element is applied to the flat style display, the stability of the emitting characteristics of 20,000 to 50,000 hours under the condition of the normal frequency drive (30 to 60 Hz) shall be required, and in detail, it is necessary to keep the change of the emitting starting voltage to be within 10 voltage and the deterioration of the luminance at the drive voltage to be within 20%. However, concerning the thin film EL element which shall use material with the exception of ZnS related material and Eu contained CaS, especially the thin film EL element, which shall use the material of alkaline earth metallic sulfide, which shall contain the rare earth metal with the exception of Eu, which is the necessary material to have in order to make multi color display, it shall not satisfy the abovementioned conditions, and there was a problem in the stability. For example, the stability of the thin film EL element which shall have Ce contained SrS as the EL emission layer, has been reported, however, this thin film EL element shall

indicate the problems in the luminance and the emitting starting voltage (SID 89 Digest P. 321 or Spuringer Proceedings in Physics Vol. 38 Electro Luminescence P.132, etc.).

[Problem to be solved by the invention]
The purpose of this invention is to accomplish the stability of the long hour use concerning the thin film EL element which shall have rare earth metal with the exception of Eu added Alkaline earth metallic sulfide for the EL emission layer.

[Method of how to solve the problems]
In order to solve the abovementioned problems, the inventors of this invention had examined them diligently, and it was discovered that the thin film EL element with the stability of the long hour use can be obtained by using the emission layer which is composed of P added rare metal contained alkaline earth metallic sulfide as the host material, and by regulating the P density and the density of the rare metal within the host material. Upon the discovery of the above, this invention was able to be completed. Therefore, this invention is concerning the thin film EL element which shall be made by applying the voltage to the EL emission layer, and the said EL emission layer, it is the thin film EL element, which shall be characterized by having such EL emission layer, which shall have MgS, CaS, SrS or BaS as the host material, which shall contain the thin film, which is composed of P and at least one kind of selected rare earth metal, which are La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and having the total density of the abovementioned rare earth metal within the said thin film to be 0.03 to 3.0 atm%, and having the density of P to be 1.3 to 4.0 times of the total density of the abovementioned rare earth metal. The thin EL element of this invention shall be characterized by having an unique EL emission layer, and this emission layer shall have the alkaline earth metallic sulfide of MgS, CaS, SrS or BaS as the host material, and the rare earth metal and P contained thin film shall be contained within the host material, and also, P density and the density of the rare earth metal within the said thin film is regulated. The EL emission layer which shall contain the thin film, which shall contain P and the rare earth metal within the host material, shall mean that the EL emission layer shall only be composed of the abovementioned thin films, and/or the EL emission layer shall be composed of the laminated layer of the thin film and other film, etc. Also, concerning this invention, the density of the rare earth metal within the host material shall be regulated depending on the total atom number of the number of atoms of the rare earth metal / within the host material. Due to the reason that the EL emission layer shall contain the abovementioned thin film, the thin film EL element of this invention shall indicate the stability concerning the luminance. Further, although the reason is not confirmed, the atom number of each rare earth metal with the exception of Eu is 3, and the alkaline earth metallic loss, which shall be generated when such rare earth metal is contained to the alkaline earth sulfide, shall disappear because of P, and also, it is assumed that P and sulfur shall have a relatively close number of the ion radius. Also, the density of P which is contained in the EL emission layer of the thin film EL element of this invention, is preferably to be 1.5 to 3.0 times of the density of the total of the rare earth metal with the exception of Eu, and by containing within the abovementioned range of the amount, the obtained thin film EL element shall have even higher luminance and longer life.

Also, concerning the thin film EL element of this invention, especially concerning the thin film EL element which shall have the EL emission layer, which shall have CaS as the host material, Ce and P shall contain within the said host material, the density of Ce within the said thin film is to be 0.03 to 0.4 atm% and P density is to be 1.3 to 4.0 times of the density of the abovementioned Ce, it shall indicate stable green color emitting with high luminance, and concerning the thin film EL element, which shall have the EL emission layer, which shall have SrS as the host material, Ce and P shall contain within the said host material, the density of Ce within the said thin film is to be 0.03 to 0.4 atm% and P density is to be 1.3 to 4.0 times of the density of the abovementioned Ce, it shall indicate stable blue color emitting with high luminance. Further, the thin film EL element and the EL emission layer which the EL emission layer shall have SrS as the host material, thin films of Ce, Eu and P shall be contained to, Ce density within the thin film is to be 0.04 to 0.4 atm%, Eu density is to be 0.01 to 0.03 atm% and P density is to be 1.3 to 4.0 times of the density of the abovementioned Ce, shall be laminated with the thin film, which shall have SrS as the host material and shall contain Ce and P within the host material, and the ZnS thin film, which shall contain Mn as the layer. The Ce density within the thin film which shall have the host material as SrS and shall structure the abovementioned layer, shall be 0.03 to 0.4 atm%, P density shall be 1.3 to 4.0 times of the abovementioned Ce density, and Mn density (Atom number of Mn / Total atom number within the ZnS thin film) within the abovementioned ZnS thin film shall be 0.1 to 1.0 atm%. Such thin film EL element shall produce stable white emitting, and therefore, by laminating the color filter, the thin film EL element which can indicate multi color display can be obtained.

The structure of the thin film EL element of this invention shall not be limited if it contains the abovementioned EL emission layer and has the method to apply voltage to the said EL emission layer, and such example structure is shown in Figure 1. Concerning Figure 1, voltage shall be applied to the EL emission layer 4 through the transparent electrode 2 and the rear electrode 6. Also, although the thickness of the emission layer related to the thin film EL element of this invention shall not be specially limited, it is preferable to make it between 0.5 to 2.5 μm considering the brightness and the drive voltage of the thin film EL element.

The EL emission layer of the thin film EL element of this invention shall be created by different kinds of the thin film forming techniques such as the sputtering method, the deposition technique, CVD method, MOCVD method and ALE method, etc. Among those forming techniques, in the case of using the deposition technique to create the EL emission layer, the rare earth metal and P added vapor source shall be used as the sulfide, which is used for the host material of the EL emission layer, and the addition of P to the vapor source can be made by adding varieties of phosphide such as phosphate, red phosphorus and strontium phosphide, etc., however, especially the use of $NH_4H_2PO_4$ is preferred, and by using this, the adjustment of P density within the EL element shall become easy.

Also, it is preferable to perform heat treatment at 400 to 700 °C within either vacuum atmosphere or inert gas atmosphere after forming is completed no matter which method is used for such forming, and by doing this, the stability of the emitting characteristics of the thin film EL element which is obtained by the forming, shall be improved.

[Example of implementation]
Herebelow, the implementation examples of this invention shall be shown, however, this invention shall not be limited to those examples.

(Implementation example 1)
The thin film EL element, which is shown in Figure 1, was created as follows. First of all, the stripe shaped transparent electrode 2 was created by the photo etching method on top of the glass substrate 1, then the first insulation layer 3 was created on top of them. The first insulation layer 3 was created by laminating SiO_2 thin film of the thickness of 0.03 μm and Si_3N_4 thin film by the RF sputtering method. Next, EL element 4 of the thickness of approximately 1.1 μm was created on top of the first insulation layer 3. The EL emission layer 4 was created by the electron beam deposition technique using the pellet, which was molded by mixing Ce_2S_3 of 0.08 atm% and $NH_4H_2PO_4$ to SrS, as the vapor raw material. As for the condition of the deposition, the substrate temperature was fixed at 650 °C, the reachable vacuum condition was made less than 3 x 10^{-6}Torr, the atmosphere during the deposition was controlled by introducing hydrogen sulfide of 1 x 10^{-4}Torr, and the accumulation speed was set as 5 Å / sec. As for the result of this, Ce density within the EL emission layer became 0.09 atm%. Further, P density within the EL emission layer was adjusted by changing the containing amount of $NH_4H_2PO_4$ within the vapor raw material. After that, the second insulation layer 5 was created by laminating 0.15 μm of Si_3N_4 thin film and 0.05 μm of $SrTa_2O_6$ thin film using the RF sputtering method on top of the EL emission layer 4, and further, on top of this, 0.1 μm of the metal Al was created at the straight crossing position with the transparent electrode as the rear electrode 6, and then the thin film EL element was completed.

Next, the characteristics test of the obtained thin film EL element was performed. In order to perform the characteristics test, the rear glass was attached to the thin film EL element to prevent humidity, and the injection space was sealed by inserting silica gel contained silicon oil from the injection space between the said rear glass and the thin film EL element. Also, the characteristics test was performed by applying sine wave voltage of 1 KHz between the transparent electrode 2 and the rear electrode 6 in order to measure luminance, etc., the aging for measuring the life span of the thin film EL element was performed by applying the voltage, which was 50 V higher than the initial emitting starting voltage, at the drive frequency of 5KHz. Further, the condition of this aging was acceleration of approximately 100 to 200 times compared to the normal element drive condition.

As for the characteristics test, aging determination of the luminance (L_{60}) was performed at the voltage, which was 60 V higher than the emitting starting voltage of the initially obtained thin film EL element. Also, as for the elapsed time, the aging of the thin film EL element was performed. The determination result is shown in Figure 2 (the initial

luminance is standardized as 1.0). As for the result of the determination, it was discovered that concerning the thin film EL element which shall contain the EL emission layer, which shall contain at least 0.12 atm% of P, at least 80% of the initial luminance was maintained even after the aging of 300 hours, and especially in the case of containing P amount of 0.23 atm%, at least 80% of the initial luminance level was maintained even after the aging of 1000 hours.

Figure 3 shows the variation of the emitting starting voltage of after 300 hours compared to the aging of after 10 hours. The variation of the emitting starting voltage of the thin film EL element which shall contain the EL emission layer which shall contain at least 0.10 atm% of P was within 10 V, and especially concerning the trial material which shall contain at least 0.17 atm% of P, the variation of the emitting starting voltage was within 4 V, which was fairly good.

Figure 4 shows the dependency of the chromaticity coordinates against P density within the EL emission layer. Together with the increase of P density, the chromaticity coordinates was shifted to the blue color side. Also, according to the absolute value of the luminance of the thin film EL element, as it is shown in Figure 5, the thin film EL element, which shall have the EL emission layer, which does not contain P, was high during the initial period, and after 24 hour aging, the thin film EL element, which shall have the EL emission layer, which contains 0.1 to 0.2 atm% of P density, indicated the highest number.

(Implementation example 2)
The thin film EL element was created using the same method as the implementation example 1. However, the Ce density within the EL emission layer was made between 0.1 and 0.5 atm%, the ratio of Ce and P was made 1 to 3, then several kinds of the thin film EL elements were created. Next, L_{60} was measured after performing 300 hour aging at 5 KHz to the obtained thin film EL element. As for the result of this, when P / Ce is more than 1.3, and after the 300 hour aging was performed, luminance of at least 80% of the initial number was maintained. Figure 6 shows the dependency toward the ratio between P and Ce (P / Ce) of L_{60} (The initial luminance was standardized as 1.0).

Also, the initial luminance of the obtained thin film EL element was measured. Figure 7 shows the dependency of the initial luminance against Ce density within the EL emission layer of the case when P / Ce is 2. The highest initial luminance was indicated when the Ce density within the EL emission layer was 0.1 to 0.2 atm%, and it became less than the half when it exceeded 0.4 atm%.

(Implementation example 3)
The thin film EL element was created using the same method as the implementation example 1. However, after the emission layer 4 was deposited making the Ce density within the EL emission layer to be 0.1 atm% and P density within the EL emission layer to be 0.2 atm%, heat treatment was applied for one hour at 600 °C within the vacuum atmosphere of 5×10^{-6} Torr in order to create the thin film EL element. Also, at the same

time, for the comparison purpose, the thin film EL element which shall not apply heat treatment was also created.

Figure 8 compares the aging of luminance – voltage characteristics of the trial material of when the heat treatment was not applied (a) and when the heat treatment was applied (b). In the case of the thin film EL element which the heat treatment was not applied, after 31 hour aging, together with the increase of the emitting starting voltage, the incline of the luminance – voltage characteristics decreased gradually, and therefore, although the aging of L_{60} was approximately 10% between 31 hours and 300 hours, the luminance at the fixed voltage became lower by approximately 20%. Compared to this, as for the thin film EL element, which the heat treatment was applied, after 31 hour aging, although the emitting starting voltage was increased a little, luminance – voltage characteristics was shifted almost parallel. Because of this, there were almost no change in L_{60} between 31 hours and 300 hours, and the change of the luminance at the fixed voltage was even within 10%.

(Implementation example 4)
The thin film EL element was created using the same method as the implementation example 1. However, after depositing the EL emission layer 4, which shall have CaS as the host material making Ce density to be 0.1 atm%, P density to be 0 atm% and 0.2 atm%, heat treatment was performed for one hour at 600 °C within the vacuum atmosphere of 5×10^{-6}Torr. L_{60} after applying 300 hour aging at 5 KHz to the obtained element was 20% when the P density was 0 atm% against the initial L_{60}, and was 95% in the case of 0.2 atm%. This element indicated the green color emitting with high luminance.

(Implementation example 5)
The thin film EL element was created using the same method as the implementation example 1. However, after depositing the EL emission layer 4 making Pr as the rare earth metal, which shall be added to SrS, Pr density to be 0.1 atm%, P density to be 0 atm% and 0.2 atm%, heat treatment was performed for one hour at 600 °C within the vacuum atmosphere of 5×10^{-6}Torr. The initial L_{60} of this element indicated almost the same value when P density within the EL emission layer was 0 atm% and when P density within the EL emission layer was 0.2 atm%. Also, L_{60} after applying 300 hour aging at 5 KHz was decreased to 55% when the P density against the initial L_{60} was 0 atm%. On the other hand, when the P density was 0.2 atm%, luminance suddenly kept increasing after aging until 20 hours, and L_{60} became 150% of the initial L_{60}, and the luminance kept increasing even after that, but gradually, then L_{60} after 300 hour aging became 165% of the initial L_{60}. Also, the variation of the emitting starting voltage was within 7 V after applying 300 hour aging regardless of the P density.

From the aforementioned result, concerning the thin film EL element which shall have the EL emission layer, which shall contain Pr and P within the host material of SrS, it was discovered that the luminance shall increase by adding P to the emission layer and the stability shall be given by aging. Further, this element indicated the white color

emitting with spectrum which shall have the relationship of the complementary color, which shall have high luminance.

(Implementation example 6)
The thin film EL element was created using the same method as the implementation example 1. However, after depositing the EL emission layer 4 making Tb as the rare earth metal, which shall be added to SrS, Tb density to be 1.0 atm%, P density to be 0 atm%, 1.5 atm% and 2.5 atm%, heat treatment was performed for one hour at 600 °C within the vacuum atmosphere of 5 x 10^{-6}Torr. L_{60} of this element, after applying 300 hour aging at 5 KHz, was 25% when the P density was 0 atm%, 83% when the P density was 1.5 atm% and 90% when the P density was 2.5 atm%. This element indicated the green color emitting with high luminance.

(Implementation example 7)
The thin film EL element was created using the same method as the implementation example 1. However, after depositing the EL emission layer 4 making Ce and Eu as the rare earth metal, which shall be added to SrS, Ce density to be 0.1 atm%, Eu density to be 0.02 atm% and P density to be 0 atm%, 0.13 atm% and 0.2 atm%, the heat treatment was performed for one hour at 600 °C within the vacuum atmosphere of 5 x 10^{-6}Torr. L_{60} of this element, after applying 300 hour aging at 5 KHz, was 32% when the P density was 0 atm% against the initial L_{60}, 82% when the P density was 0.13 atm% and 98% when the P density was 0.2 atm%. This element indicated the white emitting with wide spectrum of between 450 and 700 nm and had high luminance. Further, by combining the color filter of red, green and blue with this thin film EL element, good red, green and blue emitting was obtained.

(Implementation example 8)
The thin film EL element was created using the same method as the implementation example 1. However, 0.5 μm of ZnS thin film, which contains 0.4 atm% of Mn was created by the electron beam deposition technique previously making the substrate temperature to be 230 °C in order to make the emission layer 4 having 2 layered structure, then on top of this thin film, another thin film, which contains Ce and P within the host material, which is SrS, was laminated. Further, the thin film which shall have SrS as the host material was created at the hydrogen sulfide atmosphere of 1 x 10^{-4}Torr making the substrate temperature to be 650 °C, and was created by depositing the thickness of 1.0 μm in order to make the Ce density 0.1 atm%, P density 0 atm% and 0.2 atm%, then the heat treatment was performed for one hour at 600 °C within the vacuum atmosphere of 5 x 10^{-6}Torr. L_{60} of this element, after applying 300 hour aging at 5 KHz, was 50% when the P density was 0 atm% and 96% when the P density was 0.2 atm%. This element indicated the white emitting with wide spectrum between 450 and 600 nm, which shall have high luminance, initially. Concerning the emitting color after 300 hour aging, in the case of the P density was 0 atm%, the emitting from the SrS thin film which shall contain Ce, became extremely weak, and it became yellow orange color, which was the same emitting color as Mn contained ZnS thin film. Compared to this, when the P density was 0.2 atm%, even after 300 hours, the emitting color was almost the same, and it produced good white emitting, and by combining the color filter of red, green and blue

with this EL element, emitting of good red, green and blue, which also has high luminance, was obtained.

[Effectiveness of the invention]
As it is mentioned in the above, the thin film EL element of this invention shall have the kind of EL emission layer which is composed of alkaline earth metallic sulfide, which shall contain the rare earth metal, which shall indicate either RGB emitting or white color emitting, which can be used for the multi color display, and it accomplished the stability for long hours. Therefore, by using the thin film EL element of this invention, the multi color emitting EL element, which shall be reliable for long hours, can be actualized.

4. Simple explanation of the figures
Figure 1 is a cross section drawing of indicating one example of the structure of the thin film EL element of this invention.

Figure 2 is a figure to indicate the result of the measurement of aging of L_{60} of the thin film EL element of this invention, which was performed in the implementation example 1.

Figure 3 is a figure to indicate the result of the measurement of the variation of the emitting starting voltage after 300 hours compared to after 10 hour aging result of the thin film EL element of this invention which was performed in the implementation example 1.

Figure 4 is a figure to indicate the chromaticity coordinates of the thin film EL element of this invention, which was created in the implementation example 1.

Figure 5 is a figure to indicate the result of the measurement of the luminance at the initial period of aging, after 24 hours and after 300 hours concerning the thin film EL element, which was performed in the implementation example 1.

Figure 6 is a figure to indicate the result of the measurement of L_{60} after 300 hour aging and the initial L_{60} of the thin film EL element of this invention, which was performed in the implementation example 2.

Figure 7 is a figure to indicate the result of the measurement of the initial luminance of the thin film EL element of this invention, which was performed in the implementation example 2.

Figure 8 is a figure to indicate the result of the measurement of the aging of luminance – voltage characteristics of the thin film EL element of this invention, which was performed in the implementation example 3. Within the figure, (a) indicates the measurement result of the element, which the heat treatment was not applied to during the forming process of the EL emission layer, and (b) indicates the measurement result of the element which the heat treatment was applied to.

Figure 1

Figure 2
Vertical: Luminance L_{60}
(The initial luminance = 1.0)
Horizontal: Elapsed time (hour)

Within the figure:
(P shall indicate P density atm%)

Figure 4
Numbers in the figure shall indicate P density (atm%)

Figure 3
Vertical: Variation of the emitting starting voltage (V)
Horizontal: P density (atm%)

Figure 5
Vertical: Luminance L_{60} (cd/m^2)
Horizontal: P density (atm%)

Within the figure:
(from the left; Initial time, after 24 hours after 300 hours)

Figure 6
Vertical: Luminance L_{60}
(The initial luminance = 1.0)
Horizontal: Atom ratio of P / Ce

Figure 7
Vertical: Luminance L_{60} (cd/m^2)

Figure 8
(a) Trial material without heat treatment
Within the figure:
(from the top; 0 hour, 31 hours, 120 hours, 320 hours)

Vertical: Luminance L_{60} (cd/m^2)
Horizontal: Voltage (V)

(b) Trial material with heat treatment for one hour at 600 °C
Within the figure:
(from the upper right; 300 hours, 121 hours, 31 hours, 0 hour)

Vertical: Luminance L_{60} (cd/m^2)
Horizontal: Voltage (V)